From Form to Function – Fabricating Functional Porphyrins

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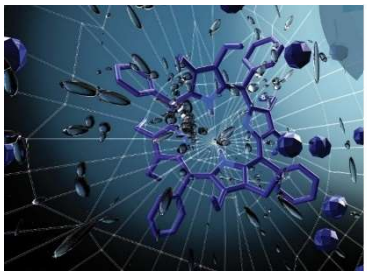
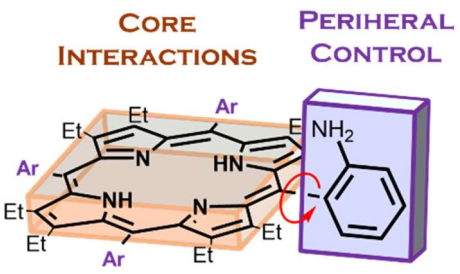
Porphyrins are nature's cofactors par excellence. Next to oxygen transport and storage, their role in electron transport and as photosynthetic pigments, they catalyze a multitude of chemical reactions. All these catalytic functions depend on the presence of a central metal which is intricately involved in the catalytic processes. However, upon appropriate manipulation of the porphyrin macrocycle conformation, the core nitrogen atoms in free base porphyrins can be involved in organocatalysis as well, indicating a new mode of catalytic action for porphyrins which does not require a central metal ion. [1] In addition, similar concepts of molecular engineering the molecular shape (form) [2] of porphyrins can be used to develop switchable porphyrin receptors for the detection of analytes and removal of pollutants. [3]





Further engineering of functional porphyrin materials is possible through control of peripheral substituents in porphyrin atropisomers and picket fence porphyrins [4] and the logical spatial construction of 1D, 2D, 3D arrays. [5] The latter involves the use of porphyrins as photoactive components together with rigid hydrocarbon linker groups such as cubane or bicyclo(1.1.1)pentane either in solution, the solid state, or interfaces.

REFERENCES

1. Roucan, M.; Kielmann, M.; Connon, S. J.; Bernhard, S. S. R.; Senge, M. O. *Chem. Commun.* **2018**, *54*, 26-29.
2. Kingsbury, C. J.; Senge, M. O. *Coord. Chem. Rev.* **2021**, *431*, 213760.
3. Kielmann, M.; Senge, M. O. *Angew. Chem. Int. Ed.* **2019**, *58*, 418-441; Norvaiša, K.; Flanagan, K. J.; Gibbons, D.; Senge, M. O. *Angew. Chem. Int. Ed.* **2019**, *58*, 16553-16557.
4. Norvaiša, K.; Gibbons, D. J.; Senge, M. O. *Chem. Eur. J.* **2021**, *27*, 331-339; Norvaiša, K.; Yeow, K.; Twamley, B.; Roucan, M.; Senge, M. O. *Eur. J. Org. Chem.* **2021**, 1871-1882; Norvaiša, K.; Maguire, S.; Donohoe, C.; O'Brien, J. E.; Twamley, B.; Gomes-da-Silva, L. C.; Senge, M. O. *Chem. Eur. J.* **2022**, *28*, e202103879.
5. Bernhard S. S. R.; Locke, G. M.; Plunkett, S.; Meindl, A.; Flanagan, K. J.; Senge, M. O. **2018**, *24*, 1026-1030; Grover, N.; Locke, G. M.; Flanagan, K. J.; Beh, M. H. R.; Thompson, A.; Senge, M. O. *Chem. Eur. J.* **2020**, *26*, 2405-2416.